# **Supporting Information**

# Xanthate-Mediated Synthesis of (*E*)-Alkenes by Semi-Hydrogenation of Alkynes Using Water as the Hydrogen Donors

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## A. General methods

Unless otherwise noted, all commercial materials and solvents were used without further purification. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> at 400 MHz (or 600 Hz) and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> at 100 MHz (or 150 Hz) respectively, <sup>1</sup>H and <sup>13</sup>C NMR were referenced to CDCl<sub>3</sub> at  $\delta$  7.260 and 77.0 respectively. The different types of carbon in the structures have been identified by HSQC, HMBC and DEPT techniques. GC–MS was obtained using electron ionization. HRMS was carried out on a MAT 95XP (Thermo). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF<sub>254</sub>), and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals. Commercial reagents were used without further purification.

## **B.** Optimization of reaction conditions

**Table S1**. Optimization of reaction conditions<sup>*a*, *b*</sup>



Entry	"Sulphur" source	Solvent	Yield <sup>b (%)</sup>
1	-	DMF	n.r.
2	Thiourea	DMF	trace
3	Copper Dimethyldithiocarbamate	DMF	trace
4	Thioacetamide	DMF	16
5	Dimethylammonium	DMF	7
	dimethyldithiocarbamate		
6	Sodium dimethyldithiocarbamate	DMF	32
7	EtOCS <sub>2</sub> K	DMF	98
8	Potassium isopropyl xanthate	DMF	95
9	EtOCS <sub>2</sub> K	DMSO	92
10	EtOCS <sub>2</sub> K	DMAc	90
11	EtOCS <sub>2</sub> K	NMP	75
12	EtOCS <sub>2</sub> K	xylene	n.r.
13	EtOCS <sub>2</sub> K	H <sub>2</sub> O	< 5
14°	EtOCS <sub>2</sub> K	DMF	31
15 <sup>d</sup>	EtOCS <sub>2</sub> K	DMF	90
16 <sup>e</sup>	EtOCS <sub>2</sub> K	DMF	85
17 <sup>f</sup>	EtOCS <sub>2</sub> K	DMF	<5
18 <sup>g</sup>	EtOCS <sub>2</sub> K	DMF	93
19 <sup>h</sup>	EtOCS <sub>2</sub> K	DMF	91

<sup>*a*</sup> Reaction conditions: alkyne **1** (1.0 mmol), "sulphur" source (2.0 mmol) in solvent (2.0 mL) and H<sub>2</sub>O (2 mmol) for at 130 °C for 12 h; <sup>*b*</sup> Isolated Yield; <sup>*c*</sup> Reaction was carried out at 120 °C; <sup>*d*</sup> 1.5 equiv EtOCS<sub>2</sub>K was used; <sup>e</sup> 1.0 equiv EtOCS<sub>2</sub>K was used; <sup>*f*</sup> Anhydrous condition; <sup>g</sup> TEMPO (2.0 mmol) was used. <sup>*h*</sup> BHT (2.0 mmol) was used. EtOCS<sub>2</sub>K = Potassium Ethylxanthate; TEMPO = 2,2,6,6-tetramethylpiperidinooxy; BHT = 2,6-di-tert-butyl-4-methylphenol.

## C. General methods for the synthesis of aryl alkenes

A 25 mL Schlenk tube was charged with diphenyl acetylene (178 mg, 1 mmol), EtOCS<sub>2</sub>K (320 mg, 2 mmol), DMF (2 mL) and a magnetic stirring bar. The reaction was performed for 12 h at 130 °C. After the reaction finished, the reaction mixture was diluted with ethyl acetate and passed through Celite. After evaporation of the solvent the residue was adsorbed on silica gel and the crude product was purified by column chromatography using petroleum as eluent.

## **D.** General methods for the synthesis of alkyl alkenes

A 25 mL Schlenk tube was charged with 2-(3,3-dimethylbut-1-yn-1-yl) pyridine (159 mg, 1 mmol), EtOCS<sub>2</sub>K (320 mg, 2 mmol), DMF (2 mL) and a magnetic stirring bar. The reaction was performed for 24 h at 150 °C. After the reaction finished, the reaction mixture was diluted with ethyl acetate and passed through Celite. After evaporation of the solvent the residue was adsorbed on silica gel and the crude product was purified by column chromatography using petroleum as eluent.

# **E.** Control experiment

Control experiment 1 (Scheme 5e in main text) :





Control experiment 2 (Scheme 5c in main text):



Control experiment 3 (Scheme 5d in main text):



# F. Characterization data for prepared compounds

(E)-but-1-en-1-ylbenzene (Scheme 3, 3)<sup>[1]</sup>

Ме

White liquid (103 mg, 78% yield);  $R_f = 0.74$  (petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (d, J = 7.8 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 6.38 (d, J = 16.2 Hz, 1H), 6.32 – 6.22 (m, 1H), 2.23 (dd, J = 14.4, 7.2 Hz, 2H), 1.09

(t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 137.9, 132.6, 128.7 (2C), 128.5 (2C), 126.7, 125.9, 26.1, 13.6; GC-MS (EI, 70 eV) m/z: 132, 128, 117, 104.

(E)-(5-methylhex-1-en-1-yl) benzene (Scheme 3, 4)<sup>[2]</sup>



White liquid ( 108 mg, 62% yield);  $R_f = 0.74$  (petroleum ether ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 (t, J = 8.8 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.18 (t, J = 7.0 Hz, 1H), 6.38 (d, J = 15.6 Hz, 1H), 6.22 (dt, J = 15.6, 6.8 Hz, 1H), 2.21 (dd, J = 15.2, 7.2 Hz, 2H), 1.60 (dd, J = 13.2, 6.8 Hz, 1H), 1.36 (dd, J = 15.2, 7.2 Hz, 2H), 0.96 – 0.92 (m, 3H), 0.90 (q, J = 2.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.9, 131.3, 129.5 (2C), 128.4 (2C), 126.7, 125.9, 38.5, 30.9, 27.5, 22.5 (2C); GC-MS (EI, 70 eV) m/z: 174, 131, 127, 117.

(E)-(2-cyclohexylvinyl) benzene (Scheme 3, 5)<sup>[3]</sup>



White liquid (134 mg, 72% yield);  $R_f = 0.65$  (petroleum ether ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (d, J = 7.6 Hz, 2H), 7.29 (dd, J = 15.2, 7.2 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 6.36 (d, J = 16.0 Hz, 1H), 6.20 (dd, J = 15.6, 6.8 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.78 (dd, J = 14.4, 11.2 Hz, 4H), 1.70 (d, J = 12.8 Hz, 1H), 1.37 – 1.29 (m, 2H), 1.26 – 1.16 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.0, 136.8, 128.4, 127.2(2C), 126.7 (2C), 125.9, 41.1, 32.9(2C), 26.2, 26.0(2C); GC-MS (EI, 70 eV) m/z: 186, 143, 129, 108.

(E)-(3,3-dimethylbut-1-en-1-yl) benzene (Scheme 3, 6)



White liquid (67 mg, 42% yield);  $R_f = 0.78$  (petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d, J = 7.2 Hz, 2H), 7.31 (dd, J = 7.2, 1.8 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 6.32 (d, J = 16.2 Hz, 1H), 6.27 (d, J = 16.2 Hz, 1H), 1.14 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  141.8, 138.0, 128.5 (2C), 126.7 (2C), 126.0, 124.5, 32.5, 29.6 (3C); GC-MS (EI, 70 eV) m/z: 160, 145, 128, 117; ESI-HRMS (m/z): [M+ H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>17</sub>, 161.1325, found: 161.1323.

(E)-2-(3,3-dimethylbut-1-en-1-yl) pyridine (Scheme 3, 8)



Yellow liquid (142 mg, 88% yield);  $R_f = 0.51$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.52 (dd, J = 4.8, 0.6 Hz, 1H), 7.56 (td, J = 7.8, 1.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.05 (ddd, J = 7.4, 4.8, 1.0 Hz, 1H), 6.78 (d, J = 16.2Hz, 1H), 6.41 (d, J = 16.2 Hz, 1H), 1.15 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ 156.2, 149.1, 146.0, 136.2, 124.8, 121.3, 121.0, 33.3, 29.2 (3C); GC-MS (EI, 70 eV) m/z: 161, 146, 142, 131; ESI-HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>16</sub>N, 162.1277, found: 162.1274.

(E)-3-(3,3-dimethylbut-1-en-1-yl) pyridine (Scheme 3, 9)



Yellow liquid (153 mg, 95% yield);  $R_f = 0.54$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.52 (s, 1H), 8.36 (d, J = 4.2 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.14 (dd, J = 7.8, 4.8 Hz, 1H), 6.27 (d, J = 16.2 Hz, 1H), 6.22 (d, J = 16.2 Hz, 1H), 1.08 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  147.9, 147.7, 144.0, 133.4, 132.3, 123.2, 121.1, 33.5, 29.3(3C); GC-MS (EI, 70 eV) m/z: 161, 146, 142, 131; ESI-HRMS (m/z): [M+ H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>16</sub>N, 162.1277, found: 162.1275.

(E)-4-(3,3-dimethylbut-1-en-1-yl) pyridine (Scheme 3, 10)



Yellow liquid (119 mg, 74% yield);  $R_f = 0.45$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.57 (s, 1H), 8.42 (d, J = 4.2 Hz, 1H), 7.67 (dt, J = 7.8, 7.8 Hz, 1H), 7.20 (dd, J = 7.8, 4.2 Hz, 1H), 6.32 (d, J = 16.2 Hz, 1H), 6.27 (d, J = 16.2Hz, 1H), 1.13 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  148.0, 147.7, 144.1, 133.5, 132.3, 123.2, 121.1, 33.5, 29.3(3C); GC-MS (EI, 70 eV) m/z: 161, 146, 131, 127; ESI-HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>16</sub>N, 162.1277, found: 162.1264.





White liquid (138 mg, 74% yield);  $R_f = 0.55$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.54 (d, J = 1.2 Hz, 1H), 8.42 – 8.38 (m, 1H), 7.65 (dt, J = 7.8, 1.8 Hz, 1H), 7.20 (dd, J = 7.8, 4.8 Hz, 1H), 6.31 (d, J = 16.2 Hz, 1H), 6.24 (dd, J = 15.6, 6.6 Hz, 1H), 2.17 – 2.12 (m, 1H), 1.82 – 1.75 (m, 4H), 1.70 – 1.66 (m, 1H), 1.31 (ddd, J = 12.8, 8.0, 3.2 Hz, 2H), 1.21 – 1.15 (m, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  147.9, 147.7, 139.2, 133.6, 132.4, 123.7, 123.3, 41.2, 32.7 (2C), 26.06, 25.93 (2C); GC-MS (EI, 70 eV) m/z: 187, 180, 172, 158; ESI-HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>18</sub>N, 188.1434, found: 188.1432.

(F)-3-(2-cyclopentylvinyl)pyridine (Scheme 3, 11)



Yellow liquid (67 mg, 39% yield);  $R_f = 0.43$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.52 (s, 1H), 8.38 (d, J = 4.8 Hz, 1H), 7.61 (dd, J = 7.6, 1.2 Hz, 1H), 7.16 (dd, J = 8.0, 5.2 Hz, 1H), 6.31 (d, J = 16.0 Hz, 1H), 6.23 (dd, J = 16.0, 7.2 Hz, 1H), 2.61 – 2.54 (m, 1H), 1.83 (ddd, J = 11.0, 8.0, 3.0 Hz, 2H), 1.67 (ddd, J = 8.2, 6.4, 2.4 Hz, 2H), 1.62 – 1.56 (m, 2H), 1.42 – 1.33 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.9, 147.7, 138.0, 133.4, 132.3, 124.3, 123.2, 43.8, 33.0(2C), 25.1(2C); GC-MS (EI, 70 eV) m/z: 173, 158, 144, 130; ESI-HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>16</sub>N, 174.1277, found: 174.1276.

(E)-6-(2-cyclohexylvinyl) quinoline (Scheme 3, 13)



Yellow liquid (147mg, 62% yield);  $R_f = 0.47$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.79 (dd, J = 2.4, 1.2 Hz, 1H), 8.04 – 7.96 (m, 2H), 7.78 (d, J = 8.8 Hz, 1H), 7.57 (s, 1H), 7.30 – 7.25 (m, 1H), 6.47 (d, J = 16.0 Hz, 1H), 6.37 – 6.25 (m, 1H), 2.22 – 2.10 (m, 1H), 1.86 – 1.74 (m, 4H), 1.68 (d, J = 12.4 Hz, 1H), 1.33 (dd, J = 24.8, 12.4 Hz, 2H), 1.20 (dd, J = 24.4, 12.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.5, 147.6, 138.3, 136.1, 135.5, 129.3, 128.4, 127.2, 126.5, 124.6, 121.1, 41.1, 32.7 (2C), 26.0 (2C), 25.9; GC-MS (EI, 70 eV) m/z: 237, 222, 208, 194. (E)-2-(2-cyclohexylvinyl)naphthalene (**Scheme 3, 7**) <sup>[3]</sup>



White solid (101 mg, 43% yield);  $R_f = 0.43$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (t, J = 8.8 Hz, 3H), 7.72 (s, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.51 – 7.41 (m, 2H), 6.56 (d, J = 16.0 Hz, 1H), 6.36 (dd, J = 16.0, 7.2 Hz, 1H), 2.24 (ddd, J = 17.8, 9.0, 5.4 Hz, 1H), 1.96 – 1.81 (m, 4H), 1.76 (d, J = 12.8 Hz, 1H), 1.41 (dd, J = 24.7, 12.3 Hz, 2H), 1.33 – 1.23 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 

137.3, 135.6, 133.8, 132.7 (2C), 128.0, 127.8, 127.6, 127.4, 126.0, 125.3, 123.6, 41.3, 33.0(2C), 26.2, 26.1 (2C); GC-MS (EI, 70 eV) m/z: 236, 221, 193, 179.

(E)-1-methyl-5-(4-methylpent-1-en-1-yl)-1H-pyrazole (Scheme 3, 14)



Yellow liquid ( 70 mg, 43% yield);  $R_f = 0.39$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (d, J = 1.8 Hz, 1H), 6.27 (d, J = 1.8 Hz, 1H), 6.25 – 6.22 (m, 1H), 6.15 (dt, J = 16.2, 15.0 Hz, 1H), 3.83 (s, 3H), 2.10 (td, J = 7.2, 1.2 Hz, 2H), 1.72 (td, J = 13.2, 6.6 Hz, 1H), 0.94 (s, 3H), 0.93 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  141.0, 138.2, 134.2, 117.5, 102.2, 42.5, 36.4, 28.3, 22.3(2C); GC-MS (EI, 70 eV) m/z: 163, 149, 133, 121; ESI-HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>10</sub>H<sub>17</sub>N<sub>2</sub>, 165.1386, found: 165.1385.

(E)-oct-4-ene (Scheme 3, 15)<sup>[5]</sup>

Me

White liquid (36 mg, 32% yield); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  5.39 (ddd, J = 5.2, 3.7, 1.6 Hz, 2H), 2.00 – 1.90 (m, 4H), 1.36 (dq, J = 14.7, 7.4 Hz, 4H), 0.88 (t, J = 7.4 Hz, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  130.3 (2C), 34.7 (2C), 22.7 (2C), 13.6 (2C). GC-MS (EI, 70 eV) m/z: 112, 83, 70, 55, 41.

1-chloro-4-vinylbenzene (Scheme 3, 16)<sup>[6]</sup>

Yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.27 (m, 4H), 6.67 (dd, J = 17.6, 10.9 Hz, 1H), 5.72 (d, J = 17.6 Hz, 1H), 5.27 (d, J = 10.9 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.1, 135.7, 133.4, 128.7 (2C), 127.4 (2C), 114.4. GC-MS (EI, 70 eV) m/z: 140, 138, 112, 103, 77.

(E)-1,2-diphenylethene (Scheme 4, 2)<sup>[7]</sup>



White solid (176 mg, 98% yield);  $R_f = 0.64$  (petroleum ether); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.50 (d, J = 8.0 Hz, 4H), 7.34 (t, J = 7.6 Hz, 4H), 7.23 (dd, J = 14.0, 7.2 Hz, 2H), 7.10 (s, 2H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.3 (2C), 128.7 (4C), 127.6 (4C), 126.5 (4C); GC-MS (EI, 70 eV) m/z: 180, 165, 152, 126.

(E)-1-methyl-4-styrylbenzene (Scheme 4, 18)<sup>[7]</sup>



White solid (176 mg, 91% yield);  $R_f = 0.67$  (petroleum ether); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H), 7.31 – 7.22 (m, 2H), 7.18 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 7.6 Hz, 2H), 6.99 (d, J = 18.4 Hz, 2H), 2.29 (s, 3H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.45, 137.36, 134.5, 129.3 (2C), 128.6(4C), 127.6 (2C), 127.3, 126.4, 126.4, 21.2 ;GC-MS (EI, 70 eV) m/z: 194, 179, 165, 115 .

(E)-1-(tert-butyl)-4-styrylbenzene (Scheme 4, 19)



White solid (217 mg, 92% yield);  $R_f = 0.59$  (petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 – 7.49 (m, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.40 (dd, J = 9.6, 2.4 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.17 – 7.00 (m, 2H), 1.35 (d, J = 3.0 Hz, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  150.7, 137.5, 134.5, 128.6 (2C), 128.5 (2C), 127.9 (2C), 127.4, 126.4, 126.2, 125.6 (2C), 34.6, 31.3, 31.3(2C); GC-MS (EI, 70 eV) m/z: 236, 221, 193, 178; ESI-HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>21</sub>, 237.1638, found: 237.1637.

(E)-trimethyl(4-styrylphenyl) silane (Scheme 4, 20)<sup>[8]</sup>



White solid (219 mg, 87% yield);  $R_f = 0.71$  (petroleum ether ); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, J = 7.8 Hz, 2H), 7.67 (d, J = 7.8 Hz, 4H), 7.50 (t, J = 7.8 Hz, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 16.8 Hz, 1H), 7.27 (d, J = 16.8 Hz, 1H), 0.49 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  139.8, 137.7, 137.3, 133.6 (2C), 128.9 (2C), 128.6 (2C), 128.6, 127.6 (2C), 126.5, 125.8, 1.1 (3C); GC-MS (EI, 70 eV) m/z: 252, 237, 207, 191.

(E)-3-styrylphenol (Scheme4, 21)<sup>[4]</sup>



white solid (186 mg, 95% yield);  $R_f = 0.47$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 7.31 – 7.11 (m, 3H), 7.05 (dd, J = 12.8, 8.0 Hz, 3H), 6.99 (s, 1H), 6.74 (d, J = 7.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.8, 139.0, 137.1, 129.8, 129.1 (2C), 128.6 (2C), 128.2, 127.7, 126.5, 119.3, 114.7, 113.0; GC-MS (EI, 70 eV) m/z: 196, 177, 165, 152 .

(E)-1-methoxy-4-styrylbenzene (Scheme 4, 22)<sup>[7]</sup>



White solid (189 mg, 90% yield);  $R_f = 0.67$  (petroleum ether ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 (t, J = 5.0 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.33 (t, J = 7.8 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.06 (d, J = 16.4 Hz, 1H), 6.96 (d, J = 16.4 Hz, 1H), 6.91 – 6.87 (m, 2H), 3.81 (s, 3H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.3, 137.6, 130.1 (2C), 128.6,

128.2 (2C), 127.7 (2C), 127.2, 126.6, 126.2, 114.1 (2C), 55.3 ; GC-MS (EI, 70 eV) m/z: 210, 195, 179, 139 .

(E)-4-styrylaniline (Scheme 4, 23)<sup>[7]</sup>

Gray solid (168 mg, 860% yield);  $R_f = 0.62$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (d, J = 7.6 Hz, 2H), 7.35 (s, 2H), 7.34 – 7.26 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 16.4 Hz, 1H), 6.93 (d, J = 16.4 Hz, 1H), 6.68 (d, J = 8.4 Hz, 2H), 3.74 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  146.1, 137.9, 128.7 (2C), 128.6 (2C), 128.0 (2C), 127.7, 126.9, 126.1, 125.1, 115.2 (2C); GC-MS (EI, 70 eV) m/z: 195, 180, 165, 139.

(E)-3-styrylaniline (Scheme 4, 24)<sup>[7]</sup>



Gray solid (181 mg, 93% yield);  $R_f = 0.42$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.58 – 7.39 (m, 2H), 7.35 (dd, J = 7.2, 1.6 Hz, 2H), 7.26 – 7.18 (m, 1H), 7.13 (dd, J = 15.6, 7.6 Hz, 1H), 7.12 – 6.94 (m, 2H), 6.95 (t, J = 14.4 Hz, 1H), 6.91 – 6.71 (m, 1H), 6.70 – 6.33 (m, 1H), 3.65 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  146.6, 138.4, 137.4, 129.6 (2C), 128.9 (2C), 128.6, 128.5, 127.5, 126.5, 117.3, 114.7, 112.9; GC-MS (EI, 70 eV) m/z: 195, 178, 165, 152 .

(E)-4,4,5,5-tetramethyl-2-(4-styrylphenyl)-1,3,2-dioxaborolane (Scheme 4, 25)<sup>[8]</sup>



White solid (290 mg, 95% yield);  $R_f = 0.32$  (ethyl acetate/petroleum ether = 1: 10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (d, J = 8.0 Hz, 2H), 7.54 – 7.45 (m, 4H), 7.32 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.08 (d, J = 16.4 Hz, 1H), 1.33 (s, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.0, 137.1, 135.1 (2C), 129.6, 128.6 (2C), 128.6 (2C), 127.7, 126.6 (2C), 125.8 (2C), 83.7 (2C), 24.8 (4C); GC-MS (EI, 70 eV) m/z: 306, 291, 233, 220.

(E)-1-chloro-4-styrylbenzene (Scheme 4, 26)<sup>[7]</sup>



white solid (184 mg, 86% yield);  $R_f = 0.58$  (petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (d, J = 7.8 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 16.2 Hz, 1H), 7.06 (d, J = 16.2 Hz, 1H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  137.0, 135.8, 133.1, 129.3 (2C), 128.8 (2C), 128.7 (2C), 127.8 (2C), 127.6, 127.3, 126.5 ; GC-MS (EI, 70 eV) m/z: 214, 178, 152, 115 .

(E)-1-bromo-4-styrylbenzene (Scheme 4, 27)<sup>[10]</sup>



White solid (178 mg, 69% yield);  $R_f = 0.63$  (petroleum ether ); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 – 7.42 (m, 4H), 7.37 (d, J = 7.2 Hz, 4H), 7.27 (d, J = 11.4 Hz, 1H), 7.10 (d, J = 16.8 Hz, 1H), 7.03 (d, J = 16.2 Hz, 1H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  136.9, 136.3, 131.8(2C), 129.4 (2C), 128.7 (2C), 128.0 (2C), 127.9, 127.4, 126.5, 121.3 ; GC-MS (EI, 70 eV) m/z: 258, 245, 178, 163.

(E)-1-fluoro-3-styrylbenzene (Scheme 4, 28)<sup>[11]</sup>



White solid (190 mg, 96% yield);  $R_f = 0.54$  (petroleum ether); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.50 (dd, J = 3.2, 1.6 Hz, 2H), 7.36 (dd, J = 8.4, 7.2 Hz, 2H), 7.30 (dd, J = 8.0, 2.0 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.23 – 7.17 (m, 1H), 7.10 (d, J = 16.0 Hz, 1H), 7.04 (d, J = 16.4 Hz, 1H), 6.97 – 6.90 (m, 1H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.2 (d, J = 243.7 Hz, 1C), 139.8 (d, J = 7.7 Hz, 1C), 136.8, 130.07 (d, J = 8.3 Hz, 1C), 130.04, 128.7 (2C), 128.0, 127.5 (d, J = 2.6 Hz, 1C), 126.6 (2C), 122.4 (d, J = 3.0 Hz, 1C), 114.4 (d, J = 21.4 Hz, 1C), 112.8 (d, J = 16.7 Hz, 1C) ; GC-MS (EI, 70 eV) m/z: 198, 183, 177, 165 .

(E)-1-styryl-4-(trifluoromethyl) benzene (Scheme 4, 29)<sup>[7]</sup>



White solid (226 mg, 91% yield);  $R_f = 0.68$  (petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 (q, J = 8.6 Hz, 4H), 7.50 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 7.16 (d, J = 16.3 Hz, 1H), 7.08 (d, J = 16.3 Hz, 1H); <sup>13</sup>C NMR (150 MHz, DMSO)  $\delta$  148.9, 141.3, 136.9, 132.23, 129.2, 127.3 (q,  $J_{C-F} = 31.5$  Hz, 1C), 126.8 (2C), 125.8, 125.5 (q,  $J_{C-F} = 3.75$  Hz, 1C), 125.3, 123.5, 114.9, 114.4, 112.1; GC-MS (EI, 70 eV) m/z: 248, 233, 207, 179.

(E)-1-(4-styrylphenyl) ethan-1-one (Scheme 4, 30) <sup>[7]</sup>



White solid (200 mg, 89% yield);  $R_f = 0.47$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.23 (d, J = 16.4 Hz,

1H), 7.13 (d, J = 16.4 Hz, 1H), 2.60 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  197.4, 141.9, 136.6, 135.9, 131.4 (2C), 128.8 (2C), 128.7 (2C), 128.3 (2C), 127.4, 126.8, 126.4, 26.5; GC-MS (EI, 70 eV) m/z: 222, 207, 178, 152.

(E)-2-styrylnaphthalene (Scheme 4, 31)<sup>[12]</sup>



White solid (219 mg, 95% yield);  $R_f = 0.59$  (petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 (d, J = 13.2 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 6.6 Hz, 2H), 7.45 – 7.37 (m, 2H), 7.34 (s, 2H), 7.20 (dd, J = 28.2, 17.4 Hz, 3H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  137.3, 134.7, 133.6, 133.0, 128.9 (2C), 128.7 (2C), 128.7, 128.3, 128.0, 127.7, 127.6, 126.6, 126.5, 126.3, 125.8, 123.4; GC-MS (EI, 70 eV) m/z: 230, 215, 202, 189 .

(E)-1-chloro-4-(4-methylstyryl) benzene (Scheme 4, 32)

White solid (210 mg, 92% yield);  $R_f = 0.54$  (petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 (t, J = 5.6 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.33 – 7.26 (m, 2H), 7.18 (t, J = 10.0 Hz, 2H), 7.06 (d, J = 16.3 Hz, 1H), 7.00 (d, J = 16.3 Hz, 1H), 2.37 (d, J = 4.5 Hz, 3H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  137.8, 136.0, 134.2, 132.9, 129.4 (2C), 129.2 (2C), 128.8 (2C), 127.5 (2C), 126.4, 126.3, 21.3 ; GC-MS (EI, 70 eV) m/z: 228, 213, 192, 178.

(E)-1-butyl-4-(4-chlorostyryl) benzene (Scheme 4, 33)



White solid (232 mg, 86% yield); mp 137-138 °C;  $R_f = 0.68$  (petroleum ether); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (d, J = 8.0 Hz, 4H), 7.34 – 7.20 (m, 2H), 7.15 (t, J = 12.2 Hz, 2H), 7.02 (d, J = 16.4 Hz, 1H), 6.96 (d, J = 16.0 Hz, 1H), 2.59 (t, J = 7.8 Hz, 2H), 1.66 – 1.54 (m, 2H), 1.39 – 1.29 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.9, 136.0, 134.4, 132.9, 129.3 (2C), 128.8 (2C), 128.8 (2C), 127.5 (2C), 126.5, 126.5, 35.4, 33.5, 22.3, 14.0; GC-MS (EI, 70 eV) m/z: 270, 227, 191, 178;

(E)-4-(4-methylstyryl) aniline (Scheme 4, 34)<sup>[14]</sup>



Gray solid (205 mg, 98% yield);  $R_f = 0.32$  (ethyl acetate/petroleum ether = 1: 10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.6 Hz, 2H), 6.95 (q, J = 16.4 Hz, 2H), 6.68 (d, J = 8.0 Hz, 2H), 3.73 (s, 2H), 2.36 (s, 3H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)  $\delta$  145.9, 136.6, 135.1, 129.3 (2C), 128.2 (2C), 127.6 (2C), 127.6, 126.0, 125.0, 115.2 (2C), 21.2; GC-MS (EI, 70 eV) m/z: 209, 193, 165, 152.

(E)-4-(4-butylstyryl)aniline (**Scheme 4, 35**)



Gray solid (161 mg, 64% yield); mp 105-107 °C;  $R_f = 0.39$  (ethyl acetate/petroleum ether = 1: 3); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 16.2 Hz, 1H), 6.92 (d, J = 16.8 Hz, 1H), 6.68 (d, J = 7.8 Hz, 2H), 3.72 (s, 2H), 2.69 – 2.57 (m, 2H), 1.65-1.60 (m, 2H), 1.38 (dt, J = 22.8, 22.2 Hz, 2H), 0.95 (t, J = 7.5 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  145.9, 141.8, 135.3, 128.6 (2C), 128.2 (2C), 127.7 (2C), 127.6, 126.0,

125.1, 115.2 (2C), 35.4, 33.6, 22.3, 13.9; GC-MS (EI, 70 eV) m/z: 251, 208, 193, 165 ; ESI-HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>221</sub>N, 252.1747, found: 252.1744.

(E)-4-(4-methoxystyryl)aniline (Scheme 4, 36)<sup>[15]</sup>



Gray solid (180 mg, 80% yield);  $R_f = 0.38$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.94 – 6.87 (m, 4H), 6.67 (d, J = 7.8 Hz, 2H), 3.82 (s, 3H), 3.71 (s, 2H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  158.7, 145.8, 130.7(2C), 128.3, 127.4 (2C), 127.2, 126.6, 124.7, 115.2 (2C), 114.0 (2C), 55.3; GC-MS (EI, 70 eV) m/z: 225, 210, 180, 152 .

(E)-4-(4-chlorostyryl)aniline (Scheme 4, 37)<sup>[14]</sup>



Gray solid (224 mg, 98% yield);  $R_f = 0.41$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.29 – 7.23 (m, 2H), 6.97 (d, J = 16.4 Hz, 1H), 6.84 (d, J = 16.4 Hz, 1H), 6.65 (d, J = 8.4 Hz, 2H), 3.74 (s, 2H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  146.3, 136.5, 132.3, 129.3 (2C), 128.7 (2C), 127.8 (2C), 127.6, 127.2, 123.7, 115.2 (2C); GC-MS (EI, 70 eV) m/z: 229, 214, 193, 177 .

(E)-3-(4-(trifluoromethyl) styryl) aniline (Scheme 4, 38)



Yellow solid (210 mg, 80% yield);  $R_f = 0.35$  (ethyl acetate/petroleum ether = 1: 3); <sup>1</sup>H NMR (600 MHz, DMSO)  $\delta$  7.77 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 16.2 Hz, 1H), 7.15 (d, J = 16.2 Hz, 1H), 7.05 (t, J = 7.8 Hz, 1H), 6.86 – 6.71 (m,

2H), 6.56 (dd, J = 7.8, 1.2 Hz, 1H), 5.15 (s, 2H); <sup>13</sup>C NMR (150 MHz, DMSO)  $\delta =$  148.9, 141.3, 136.9, 132.3, 129.2, 127.34 (q,  $J_{C-F} = 31.5$  Hz, 1C), 126.8, 125.8 (2C), 125.5 (q,  $J_{C-F} = 3.75$  Hz, 1C), 125.3, 123.5, 114.9, 114.4, 112.1; GC-MS (EI, 70 eV) m/z: 263, 242, 227, 193; ESI-HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>13</sub>F<sub>3</sub>N, 264.0995, found: 264.0991.

(E)-4-styryl-1,1'-biphenyl (Scheme 4, 39)<sup>[7]</sup>



White solid (246 mg, 96% yield);  $R_f = 0.42$  (ethyl acetate/petroleum ether = 1: 10); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 – 7.58 (m, 5H), 7.56 – 7.51 (m, 2H), 7.47 – 7.43 (m, 2H), 7.39 – 7.33 (m, 3H), 7.30 – 7.24 (m, 2H), 7.16 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  140.6, 140.3, 137.3, 136.3, 128.8 (2C), 128.7(2C), 128.7 (2C), 128.2 (2C), 127.6 (3C), 127.3, 127.3, 126.9, 126.9, 126.5; GC-MS (EI, 70 eV) m/z: 256, 239, 207, 178.

(E)-4-(3-fluorostyryl)-1,1'-biphenyl (Scheme 4, 40)



White solid (260 mg, 95% yield); mp 170-172 °C;  $R_f = 0.69$  (petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (dd, J = 6.6, 6.0 Hz, 4H), 7.57 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.24-7.22 (m, 1H), 7.13 (d, J = 16.8 Hz, 1H), 7.09 (d, J = 16.2 Hz, 1H), 6.98 – 6.93 (m, 1H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  163.1 (d, J = 243.75 Hz, 1C), 140.5 (d, J = 25.2 Hz, 1C), 139.6 (d, J = 7.65 Hz, 1C), 135.8, 130.1 (d, J = 8.4 Hz, 1C), 129.4, 128.8 (2C), 128.7, 127.4 (d, J = 2.55 Hz, 1C), 127.37, 127.3 (2C), 127.0 (2C), 126.9 (2C), 122.4 (d, J = 2.55 Hz, 1C), 114.3 (d, J = 21.3 Hz, 1C), 112.7 (d, J = 22.5 Hz, 1C); GC-MS (EI, 70 eV) m/z: 274, 252, 220, 196 .

(E)-1,3-dimethoxy-5-(4-methoxystyryl)benzene (Scheme 4, 41)<sup>[8]</sup>



Red liquid (54 mg, 20% yield);  $R_f = 0.39$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 16.4 Hz, 1H), 6.95 – 6.88 (m, 3H), 6.68 (s, 2H), 6.40 (s, 1H), 3.84 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.9 (2C), 159.3, 139.6, 129.9 (2C), 128.7, 127.7 (2C), 126.5, 114.1 (2C), 104.3 (2C), 99.6, 55.2 (2C); GC-MS (EI, 70 eV) m/z: 270, 255, 239, 224.

(E)-3-styrylthiophene (Scheme 4, 42)<sup>[7]</sup>



White solid (171 mg, 92% yield);  $R_f = 0.57$  (petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (d, J = 7.2 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.29 – 7.24 (m, 1H), 7.24 – 7.15 (m, 2H), 7.09 (d, J = 16.2 Hz, 1H), 6.92 (d, J = 16.2 Hz, 1H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  140.0, 137.3, 128.6(2C), 128.6(2C), 127.4, 126.2, 126.1, 124.9, 122.8, 122.3; GC-MS (EI, 70 eV) m/z: 186, 171, 152, 141.

(E)-1-methyl-5-styryl-1H-pyrazole (Scheme 4, 43) <sup>[16]</sup>



White solid (151 mg, 82% yield);  $R_f = 0.46$  (ethyl acetate/petroleum ether = 1: 10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 – 7.42 (m, 3H), 7.36 (dd, J = 6.8, 5.6 Hz, 2H), 7.28 (dd, J = 7.6, 6.0 Hz, 1H), 7.01 (dd, J = 16.0, 1.6 Hz, 1H), 6.91 (dd, J = 16.0, 1.6 Hz, 1H), 6.46 (s, 1H), 3.91 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.7, 138.4, 136.4, 131.9, 128.7 (2C), 128.2 (2C), 126.4, 114.4, 102.8, 36.5; GC-MS (EI, 70 eV) m/z: 184, 168, 156, 128. (E)-5-(4-chlorostyryl)-1-methyl-1H-pyrazole (Scheme 4, 44)



White solid (166 mg, 76% yield);  $R_f = 0.39$  (ethyl acetate/petroleum ether = 1: 3 ); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (d, J = 1.8 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 16.2 Hz, 1H), 6.90 (d, J = 16.2 Hz, 1H), 6.48 (d, J = 1.8 Hz, 1H), 3.94 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  140.5, 138.5, 135.0, 133.9, 130.6, 129.0 (2C), 127.7 (2C), 115.0, 103.0, 36.6; GC-MS (EI, 70 eV) m/z: 218, 202, 190, 168; ESI-HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>12</sub>ClN<sub>2</sub>, 219.0684, found:219.0681.

(E)-2-styrylpyridine (Scheme 5, 45)<sup>[17]</sup>



White solid ( 165 mg, 91% yield);  $R_f = 0.44$  (ethyl acetate/petroleum ether = 1: 10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.59 (d, J = 4.8 Hz, 1H), 7.63 (d, J = 16.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 7.2 Hz, 3H), 7.27 (dd, J = 14.4, 7.6 Hz, 1H), 7.16 (d, J = 16.4 Hz, 1H), 7.13 – 7.07 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.5, 149.5, 136.5, 136.5, 132.7, 128.6 (2C), 128.3 (2C), 127.8, 127.0, 122.0, 122.0; GC-MS (EI, 70 eV) m/z: 181, 166, 152, 127 .

(E)-3-styrylpyridine (Scheme 5, 46)<sup>[18]</sup>



White solid (157 mg, 87% yield);  $R_f = 0.46$  (ethyl acetate/petroleum ether = 1: 10); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.72 (s, 1H), 8.48 (s, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 7.8 Hz, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.31 – 7.18 (m, 2H), 7.14 (d, J = 16.8 Hz,

1H), 7.05 (d, J = 16.8 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  148.5 (2C), 136.5, 132.5 (2C), 130.7, 128.7(2C), 128.1 (2C), 126.6, 124.8, 123.5; GC-MS (EI, 70 eV) m/z: 181, 166, 152, 139.

(E)-4-styrylpyridine (Scheme 5, 47)<sup>[19]</sup>

White solid ( 118 mg, 65% yield);  $R_f = 0.41$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.58 (d, J = 5.2 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H), 7.40 (d, J = 7.2 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.32 (s, 1H), 7.28 (t, J = 9.4 Hz, 1H), 7.01 (d, J = 16.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.0 (2C), 144.7, 136.1, 133.2, 128.8 (2C), 128.7 (2C), 127.0, 125.9, 120.8 (2C); GC-MS (EI, 70 eV) m/z: 181, 166, 152, 115 .

(E)-2-(4-chlorostyryl)pyridine (Scheme 5, 48)<sup>[17]</sup>

White solid (200 mg, 93% yield);  $R_f = 0.38$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.59 (s, 1H), 7.66 – 7.56 (m, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.12 (d, J = 17.4 Hz, 2H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  155.1, 149.6, 136.6, 135.1, 133.9, 131.3, 128.8 (2C), 128.3 (2C), 128.2, 122.2, 122.2 ; GC-MS (EI, 70 eV) m/z: 215, 186, 178, 136 ;

(E)-3-(3-methylstyryl)pyridine (Scheme 5, 49)<sup>[20]</sup>



White solid (177 mg, 92% yield);  $R_f = 0.41$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.70 (s, 1H), 8.46 (d, *J* = 4.0 Hz, 1H), 7.78 (dd, *J* = 8.0,

1.6 Hz, 1H), 7.30 (d, J = 9.6 Hz, 2H), 7.24 (dd, J = 9.2, 7.2 Hz, 2H), 7.14 – 7.06 (m, 2H), 7.02 (d, J = 16.4 Hz, 1H), 2.36 (s, 3H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.4, 148.4, 138.3, 136.5, 133.0, 132.5, 130.9, 129.0, 128.6, 127.3, 124.6, 123.8, 123.4, 21.3 ; GC-MS (EI, 70 eV) m/z: 195, 180, 152, 115 ;

(E)-3-(4-methylstyryl)pyridine (Scheme 5, 50)<sup>[21]</sup>

White solid ( 179 mg, 92% yield);  $R_f = 0.37$  (ethyl acetate/petroleum ether = 1: 5 ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.60 (d, J = 4.4 Hz, 1H), 7.67 – 7.55 (m, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 7.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.16 – 7.09 (m, 2H), 2.37 (s, 3H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.8, 149.5, 138.3, 136.5, 133.8, 132.7, 129.4, 127.0 (2C), 126.9 (2C), 121.9, 121.8, 21.3; GC-MS (EI, 70 eV) m/z: 195, 180, 167, 152 ;

### (E)-3-(4-(tert-butyl) styryl) pyridine (Scheme 5, 51)

White solid (223 mg, 94% yield); mp 83-85 °C;  $R_f = 0.49$  (ethyl acetate/petroleum ether = 1: 10); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.72 (s, 1H), 8.48 (d, J = 4.2 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.15 (d, J = 16.2 Hz, 1H), 7.03 (d, J = 16.2 Hz, 1H), 1.34 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  151.5, 148.4, 148.2, 133.8, 133.2, 132.6, 130.7, 126.4 (2C), 125.7 (2C), 124.0, 123.5, 34.7, 31.2 (3C); GC-MS (EI, 70 eV) m/z: 237, 222, 206, 194; ESI-HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>20</sub>N, 238.1590, found: 238.1589.

### (E)-3-(4-butylstyryl)pyridine (Scheme 5, 52)



White solid ( 223 mg, 94% yield);  $R_f = 0.36$  (ethyl acetate/petroleum ether = 1: 10); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.70 (s, 1H), 8.46 (d, J = 4.2 Hz, 1H), 7.79 (dt, J = 8.4, 8.4 Hz, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.25 (dd, J = 7.8, 4.2 Hz, 1H), 7.18 (d, J = 8.4Hz, 2H), 7.13 (d, J = 16.2 Hz, 1H), 7.01 (d, J = 16.2 Hz, 1H), 2.71 – 2.55 (m, 2H), 1.63-1.58 (m, 2H), 1.39-1.33 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  148.3, 148.2, 143.2, 134.0, 133.1, 132.4, 130.7, 128.8 (2C), 126.5 (2C), 123.7, 123.4, 35.3, 33.4, 22.3, 13.9; GC-MS (EI, 70 eV) m/z: 237, 194, 180, 115;

(E)-3-(4-chlorostyryl) pyridine (Scheme 5, 53) [21]



White solid (178 mg, 83% yield);  $R_f = 0.35$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.71 (s, 1H), 8.49 (s, 1H), 7.81 (s, 1H), 7.43 (s, 2H), 7.34 (s, 2H), 7.28 (s, 1H), 7.10 (d, J = 16.2 Hz, 1H), 7.03 (d, J = 16.8 Hz, 1H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  148.7, 148.4, 135.1, 133.8, 132.7, 132.6, 129.4, 128.9 (2C), 127.8 (2C), 125.4, 123.5 ; GC-MS (EI, 70 eV) m/z: 215, 180, 152, 136 .

(E)-3-(3-chlorostyryl)pyridine (Scheme 5, 54)



White liquid (2185 mg, 86% yield);  $R_f = 0.41$  (ethyl acetate/petroleum ether = 1: 10); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.63 (d, J = 129.6 Hz, 2H), 7.83 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 1.3 Hz, 1H), 7.38 (d, J = 7.2 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.27-7.25(m, 1H), 7.15 – 7.02 (m, 2H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  148.7, 148.4, 138.4, 134.7, 132.9, 130.0(2C), 129.4, 128.1, 126.4, 126.2, 124.9, 123.7 ; GC-MS (EI, 70 eV) m/z: 215, 180, 152, 127 . (E)-3-(2-(naphthalen-2-yl) vinyl) pyridine (Scheme 5, 55)



White solid ( 203 mg, 88% yield);  $R_f = 0.39$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.75 (d, J = 1.8 Hz, 1H), 8.51 – 8.44 (m, 1H), 7.83 (d, J = 3.0 Hz, 2H), 7.81 (t, J = 7.5 Hz, 3H), 7.70 (dd, J = 8.4, 1.2 Hz, 1H), 7.48-7.44 (m, 2H), 7.30 – 7.24 (m, 2H), 7.15 (d, J = 16.8 Hz, 1H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  148.4, 148.4, 134.0, 133.5, 133.2, 133.0, 132.6, 130.8, 128.4, 128.0, 127.6, 127.1, 126.4, 126.2, 125.0, 123.5, 123.2; GC-MS (EI, 70 eV) m/z: 231, 216, 202, 176 ; ESI-HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>14</sub>N, 232.1121, found: 232.1119.

(E)-4-(4-methylstyryl)pyridine (Scheme 5, 56)<sup>[13]</sup>



White solid (181 mg, 93% yield);  $R_f = 0.43$  (ethyl acetate/petroleum ether = 1: 10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.56 (d, J = 5.6 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 6.0 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 16.4 Hz, 1H), 2.37 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.1 (2C), 144.8, 138.8, 133.4, 133.1, 129.5 (2C), 126.9 (2C), 124.9, 120.7 (2C), 21.3; GC-MS (EI, 70 eV) m/z: 195, 180, 165, 128 .

(E)-2-fluoro-4-styrylpyridine (Scheme 5, 57)



White liquid (177 mg, 89% yield);  $R_f = 0.42$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (d, J = 4.8 Hz, 1H), 7.54 (d, J = 7.2 Hz, 2H), 7.40 (t,

J = 7.5 Hz, 2H), 7.34 (dd, J = 15.0, 7.2 Hz, 2H), 7.29 (d, J = 7.8 Hz, 1H), 7.02 (d, J = 16.2 Hz, 1H), 6.98 (s, 1H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  164.6 (d, J = 235.95 Hz, 1C), 150.3 (d, J = 8.4 Hz, 1C), 147.85 (d, J = 15.6 Hz, 1C), 135.6, 134.5, 129.1, 128.9 (2C), 127.2 (2C), 124.8 (d, J = 3.75 Hz, 1C), 118.6 (d, J = 3.9 Hz, 1C), 106.3 (d, J = 37.8 Hz, 1C) ; GC-MS (EI, 70 eV) m/z: 199, 178, 170, 151 .

(E)-6-styrylquinoline (Scheme 5, 58)<sup>[9]</sup>



White solid (222 mg, 96% yield);  $R_f = 0.46$  (ethyl acetate/petroleum ether = 1: 5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.88 (d, J = 3.2 Hz, 1H), 8.11 (t, J = 7.0 Hz, 2H), 8.02 – 7.94 (m, 1H), 7.77 (d, J = 15.6 Hz, 1H), 7.66 – 7.51 (m, 2H), 7.49 – 7.39 (m, 2H), 7.39 – 7.29 (m, 2H), 7.26 (s, 2H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.9, 147.9, 136.9, 135.8, 135.4, 130.1, 129.6 (2C), 128.7 (2C), 128.4, 127.9, 127.7, 127.1, 126.5, 125.8, 121.4 ; GC-MS (EI, 70 eV) m/z: 231, 216, 202, 176.

(E)-6-(4-butylstyryl)quinolone (Scheme 5, 59)



white solid (255 mg, 89% yield);  $R_f = 0.41$  (ethyl acetate/petroleum ether = 1: 10); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.94 – 8.69 (m, 1H), 8.35 – 7.95 (m, 2H), 7.92 (d, J = 8.4 Hz, 1H), 7.67 (dd, J = 51.0, 1.2Hz, 1H), 7.61 – 7.38 (m, 2H), 7.38 – 7.27 (m, 1H), 7.27 – 7.19 (m, 2H), 7.17 (d, J = 15.0 Hz, 2H),2.65-2.61 (m, 2H), 1.73 – 1.52 (m, 2H), 1.44 – 1.32 (m, 2H), 1.05 – 0.90 (m, 3H) ; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  149.8, 147.8, 142.9, 135.7, 135.6, 134.3, 130.0, 129.5, 129.0, 128.7, 128.4 (2C), 127.1, 126.7, 126.5, 125.5, 121.3, 35.3, 33.4, 22.2, 13.9; GC-MS (EI, 70 eV) m/z: 287, 244, 230, 216 ; ESI-HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>22</sub>N, 288.1748, found: 288.1745.

(E)-1,2-diphenylethene-1,2-d2 (Scheme, 2-D)<sup>[7]</sup>



White solid (164 mg, 91% yield);  $R_f = 0.51$  (petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 (dd, J = 8.0, 1.3 Hz, 4H), 7.33 (t, J = 7.7 Hz, 4H), 7.24 (dd, J = 10.6, 4.1 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  137.2 (2C), 128.6 (4C), 127.6 (4C), 126.4 (4C); GC-MS (EI, 70 eV) m/z: 182, 175, 167, 153.

(Z)-1,2-diphenylethene (Scheme 5f)



White liquid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) & 7.25-7.16 (m, 10H), 6.59 (s, 2H).

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# F <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for products



### 2.1366 2.1366 1.346 1.346 1.346 1.346 0.327 0.923 0.907 0.885

### 77.347 77.329 77.329 77.2565 77.2565 77.2565 77.169 77.169 65.369 66.263 66.263 66.263 66.223 66.223 66.223 66.223



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### 7.374 7.325 7.325 7.325 7.325 7.325 7.325 7.325 7.1797 7.1797 7.1797 7.1797 7.1797 7.1797 7.1797 7.1797 7.1797 7.1




















### 8.795 8.795 8.795 8.785 8.788 7.787 7.7787 7.7787 7.7787 7.7787 7.7787 7.7787 7.7783 7.7783 7.7783 7.7783 7.7783 7.7783 6.2439 6.2439 6.2316 6.2316 6.2316 6.273































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-1.328

90 80 fl (ppm) 



### 7.501 7.485 7.471 7.2380 7.2380 7.27380 7.27380 7.27380 7.27380 7.27380 7.27380 7.260 7.047 7.003



7,512 7,7508 7,7











### 7.1385 7.365 7.365 7.365 7.151 7.151 7.151 7.151 7.151 7.151 7.131 7.151 7.131 7.151 7.131 7.1637 6.936

































fl (ppm) 


#### - 8.719 - 8.483 - 8.483 - 8.483 - 7.7304 - 7.7352 - 7.7354 - 7.7354 - 7.7354 - 7.7354 - 7.7354 - 7.7355 - 7.75555 - 7.75555 - 7.75555 - 7.75555 - 7.75555 -















## $-8.711 \\ -8.711 \\ -8.495 \\ -7.284 \\ -7.284 \\ -7.284 \\ -7.239 \\ -7.039 \\ -7.039 \\ -7.039 \\ -7.011 \\ -7.039 \\ -7.011 \\ -$























B.882
B.882

B.883
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B.893

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B.966

B.993
B.966

B.993</t









110 100 90 f1 (ppm) 

